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Thermodynamic parameters and their variation with temperature and chain length in a number of symmetric dimeric liquid crystals

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ABSTRACT

Different thermodynamic parameters are estimated for the first time in the case of a number of symmetric dimeric liquid crystals, (DLCs), from the thermal expansion coefficient, α computed from the density data in isotropic as well as in liquid crystalline phases. Further, the parameters like the molecular free length, L_f, the molecular radius, M_r and the nonlinearity parameter, B/A are also estimated from α in the above compounds. All these parameters are obtained either with the temperature in an individual compound or either with the spacer length or with the end alkyl chain number. The results are discussed with the body of the data available on the corresponding monomers and other monomer liquid crystalline compounds. The molecular radius is estimated from both the density and the birefringence data.

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1. Introduction

Liquid crystal dimers (LCDs) discovered by Vorlander [1] are found that the transitional properties of these compounds depend both on the length of the spacer and the parity of the number of atoms in it. In contrast to the monomers, the LCDs contain two mesogenic units either identical or non-identical connected through a flexible central spacer and are called symmetric and non symmetric DLCs respectively. Further, it is also found from the earlier studies from various researchers [2–4] that there exists a remarkable difference in the mesomorphic behaviour exhibited by these group compounds viz., the DLCs and the corresponding monomers. The mesogenic properties of these DLCs depend on many factors such as size of the mesogenic unit, length of the spacer and terminal units [5–7]. The study of density measurements helps to understand the nature of phase transitions in the mesomorphic compounds at the phase transitions. By employing the density data and in turn thermal expansion coefficient many thermo dynamic parameters can be estimated. The estimation of thermodynamic parameters is mostly dealt in pure liquids, binary, ternary mixtures of liquids and liquid crystal monomers (LC) at ambient and at different temperatures [8]. To the best of our knowledge for the first time we are trying to extend the work to dimeric liquid crystals in the present manuscript.

The nature of molecular interactions in LC compounds can be studied from different phase transformations and pretransitional effects [9]. Further, the study of thermo acoustic, anharmonic parameters provides information regarding the physico-chemical behaviour of the molecules. The Moelwyn-Hughes [10] parameter is of great importance because of its close relationship with the Gruneisen parameter and some thermo-acoustic parameters. The Gruneisen parameter [11] is an important quantity of current interest that has been found very useful in studying the internal structure, molecular order, anharmonicity, and other thermo-acoustic properties of different liquids, liquefied gases etc. Moreover, the Beyer's non linearity parameter (B/A) provides information regarding physical attributes of a liquid such as internal pressure, intermolecular spacing and acoustic scattering [12]. Sehgal [13] has reported a set of relations involving the parameter B/A for the determination of molecular properties such as internal pressure, cohesive energy, effective Van der waals constant, distance of closest approach of molecules, diffusion coefficient and rotational correlation time of pure liquids such as water, alcohols and fluorocarbons.

In view of the importance of these parameters in the present manuscript the thermodynamic parameters such as reduced molar volume ($V^{\sim}$), Moelwyn–Hughes parameter (C_1), reduced compressibility (β), fraction free volume (f), etc., are estimated from volume expansion (α). In addition to these, parameters like molecular free length (L_f), molecular radius (M_r) and the nonlinearity parameter (B/A) are also estimated. As the data on symmetric DLCs is not available, the authors have carried out extensive studies on the estimation of the above parameters for number of symmetric DLCs utilizing the available dilatometric and birefringence data from the literature over the past few years. From these studies, the authors are trying to address the following aspects (1) how will these parameters vary in a particular phase of the DLC material? (2) How do these parameters behave in

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the total DLC molecule? (3) What will be the behavior of these thermodynamic parameters at and around the phase transformation? (4) What will be their behavior in a particular homologous series? That is, how does the magnitude vary with either with the spacer length, n or the end chain length, m chain number? and (5) are there any parameters that are independent of both temperature and material in DLCs like their monomer counterparts? Finally the aim is to see whether the values of these thermo dynamic parameters for the symmetric dimeric LCs are different from their corresponding monomers or not. For some of the DLCs, where there is no density data, (in the case of 3.O11O.3, 3O.12O.3, 4.O7O.4, 4.O10O.4, 4.O11O.4, 4.O12O.4, 5.O11O.5, 5.O12O.5), the value in isotropic phase is estimated following the rule that the molar volume varies around 15 to 17 × 10^{-6} mole^{-1} per CH_2 unit at $T_{IN} + 5$ values in the isotropic phase.

2. Experimental

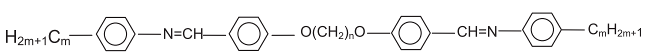
2.1. Density studies

The compounds are synthesized following the standard procedure reported in literature [14]. The crude products are repeatedly recrystallized from ethyl acetate until the transition temperatures remain constant. DSC studies are carried out using a differential scanning calorimeter (Perkin – Elmer, Diamond). Nematic and SmA phases exhibited by the compounds are identified by observing their characteristic optical textures under a polarizing microscope attached with an indigenous hot stage. The temperature resolution of the microscopic studies is ± 0.1 °C. The density measurements are carried out using a bicapillary pycnometer [5]. The capillary diameter of the pycnometer is of the order of 3.5 × 10^{-4} m and accuracy in density measurements is ± 0.1 kg m^{-3}. The permitted cooling rate was 1 °C per hour and temperature accuracy is ± 0.1 °C.

2.2. Refractive index

The refractive indices of a liquid crystal are measured with a wedge shaped glass cell, similar to the one used to obtain birefringence by Haller et al. [15], using a modified spectrometer. A wedge shaped glass cell was formed with two optically flat rectangular glass plates (50 mm × 25 mm) sandwiched with glass plate (0.4 mm) which acts as a wedge spacer. The optical flats are uniformly rubbed along the short edge to get the alignment of the LC molecule. The cell is filled with the LC material. The nematic liquid crystal in the cell acts as a uniaxial crystal with its optic axis parallel to the edge of the spacer glass plate. The temperature accuracy of the heating block was ± 0.1 °C. The accuracy in the measured refractive indices was ± 0.0005.

The molecular structure of the compounds studied is given below.



with m = 3, 4, 5, 6, 7, 8 and 10 and n = 4, 5, 6, 7, 8, 9, 10, 11 and 12.

3. Thermodynamic parameters

The procedure for the estimation of different thermodynamic parameters, molecular free length, L_f and molecular radius from both α and birefringence, δn are described in detail using the coefficient of thermal expansion (α) [16–25] is described below.

The values of coefficient of volume expansion $(\alpha) = 1/V_m\,(dV_m/dT)$ Where $dT = T_2 - T_1$, $dV_m = V_{m2} - V_{m1}$ are taken from literature [17–20] for the evaluation the following parameters.

The Moelwyns–Hughes parameter (C_1) and reduced molar volume ($V^{\sim}$) are evaluated from the following expressions.

$$C_1 = \left(\frac{13}{3}\right) + \left(\frac{1}{\alpha T}\right) + \left(\frac{4\ \alpha T}{3}\right) \tag{1}$$

$$V^{\sim} = \left\{\frac{\left(\frac{\alpha T}{3}\right)}{(1+\alpha T)} + 1\right\}^3 \tag{2}$$

The isochoric temperature coefficient of internal pressure (X) is given by

$$X = -\frac{2(1+2\,\alpha T)}{V^{\sim C_1}} \tag{3}$$

where $V^{\sim C}{}_1 = \beta$ is the reduced compressibility

Sharma parameter [17–24] S_O is given by the expression

$$S_0 = \left(-\frac{X}{2}\right)\ (3 + 4\,\alpha T). \tag{4}$$

The Huggins parameter [22] F of a liquid crystal is related to S_O by the equation

$$F = 2\left[1 + \left(\frac{S_0}{(3+4\,\alpha T)}\right)\right] - \left(3 + \frac{4\alpha T}{3}\right). \tag{5}$$

Isothermal microscopic Gruneisen parameter (Γ) is a measure of volume dependence of the hormonicity of the normal mode frequency (ν) of molecular vibrations of a material is related to F and So as

$$\Gamma = \left(\frac{2}{3}\right)\alpha T + \left(\frac{2 - F + 4\,\alpha T}{2\,\alpha T}\right). \tag{6}$$

The fraction free volume (f), is a measure of disorder due to increase of mobility of molecules in a liquid crystal and can be expressed in terms of isothermal Gruneisen parameter (Γ) as

$$f = \frac{1}{(\Gamma+1)} = \frac{V_a}{V} \tag{7}$$

where V_a is the available volume. The estimation of V_a is described below.

Thermal parameter A^* is a dimensionless parameter which shows that at low temperatures, a liquid crystal tends to be ordered, thereby makes A^* equal to unity

$$A* = 1 + \left(\frac{f}{\Gamma}\right). \tag{8}$$

The Gruneisen parameter (Γ_p) for liquid crystals can be obtained from

$$\Gamma_p = \left(\frac{2}{3}\right)\alpha T + \left(\frac{1}{2\alpha T}\right) + 2. \tag{9}$$

The isochoric acoustical parameter, Δ is given as

$$\Delta = \left(\frac{-\alpha T}{2}\right)\ . \tag{10}$$

3.1. Inter molecular free length (L_f)

The estimation of L_f is described below using the thermodynamic parameters. Using the Eqs. (1) to (3), the isothermal (K′), isochoric (K″) and isobaric (K) acoustical parameters are obtained from the following expressions

$$\begin{aligned} K' &= K + K'' \\ &= \frac{1}{2}\left[3 + \frac{(S*(1+\ \alpha T) + X)}{\alpha T}\right] \end{aligned} \tag{11}$$

$$K'' = 1 + \left(\frac{X}{2\alpha T}\right) \tag{12}$$

and

$$K = \frac{1}{2}\left[1 + \left(\frac{S*(1+\alpha T)}{\alpha T}\right)\right] \tag{13}$$

where

$$S* = 1 + \left(\frac{4\,\alpha T}{3}\right). \tag{14}$$

The isothermal acoustical parameter (K') is related to the available volume (V_a) of the compound as

$$\frac{V_a}{V_m} = \frac{1}{(K'+1)} = \frac{1}{\left(K''+K+1\right)} \tag{15}$$

where V_m is molar volume (molecular weight/density) and the available volume, (V_a) can be deduced using the thermo acoustical parameter K' as

$$V_a = \frac{V_m}{K'+1}. \tag{16}$$

Then the intermolecular free-length [24] (L_f) is given by the relation

$$L_f = \frac{2V_a}{Y} \tag{17}$$

where V_a represents the available volume per mole and Y is surface area per mole given by

$$V_0 = V - V_a \tag{17a}$$

Table 1
Variation of different thermodynamic parameters in homologous series of symmetric dimeric liquid crystals.

Comp	Phase	T °C	C_1	V~	$V\sim^{C1}$	X	X′	S_o	F	Γ	f	A*	Δ	Γ_P
3O7O3	Iso	146	9.450	1.181	4.823	−1.413	−0.586	1.121	1.311	3.806	0.208	1.055	122.77	4.558
3O8O3	Iso	182	8.535	1.220	5.474	−1.519	−0.555	1.120	1.209	3.698	0.213	1.058	126.24	4.101
3O8O3	N	160	7.442	1.305	7.241	−1.771	−0.489	1.111	0.975	3.586	0.218	1.061	105.89	3.554
3O9O3	Iso	147	8.763	1.209	5.274	−1.487	−0.564	1.121	1.239	3.724	0.212	1.057	118.43	4.215
3O9O3	N	130	8.348	1.231	5.664	−1.548	−0.547	1.120	1.181	3.677	0.214	1.058	110.15	4.007
3O10O3	Iso	168	8.068	1.249	6.008	−1.600	−0.533	1.118	1.133	3.646	0.215	1.059	117.42	3.867
3O10O3	N	150	7.468	1.302	7.170	−1.761	−0.491	1.111	0.984	3.589	0.218	1.061	103.92	3.567
3O11O3	Iso	138	8.846	1.205	5.209	−1.477	−0.567	1.121	1.249	3.734	0.211	1.057	116.51	4.256
3O12O3	Iso	152	7.506	1.298	7.068	−1.748	−0.495	1.112	0.996	3.592	0.218	1.061	105.10	3.586
4O7O4	Iso	130	8.045	1.251	6.041	−1.605	−0.531	1.118	1.128	3.644	0.215	1.059	107.05	3.856
4O8O4	Iso	169	8.841	1.205	5.213	−1.477	−0.567	1.121	1.249	3.733	0.211	1.057	125.26	4.254
4O8O4	N	154	7.883	1.263	6.289	−1.641	−0.522	1.117	1.095	3.627	0.216	1.060	111.39	3.775
4O9O4	Iso	124	9.204	1.190	4.964	−1.437	−0.579	1.121	1.288	3.777	0.209	1.055	114.91	4.435
4O10O4	Iso	154	8.905	1.202	5.165	−1.470	−0.569	1.121	1.256	3.741	0.211	1.056	121.49	4.286
4O10O4	N	140	7.449	1.304	7.221	−1.768	−0.490	1.111	0.978	3.587	0.218	1.061	101.13	3.558
4O11O4	Iso	127	8.526	1.221	5.482	−1.520	−0.555	1.120	1.208	3.697	0.213	1.058	110.91	4.096
4O12O4	Iso	139	8.373	1.229	5.636	−1.544	−0.548	1.120	1.185	3.679	0.214	1.058	112.85	4.020
5O7O5	Iso	135	9.573	1.177	4.759	−1.402	−0.589	1.121	1.321	3.822	0.207	1.054	120.23	4.620
5O8O5	Iso	172	8.963	1.200	5.123	−1.463	−0.571	1.121	1.263	3.748	0.211	1.056	127.07	4.315
5O8O5	N	154	7.546	1.293	6.967	−1.734	−0.498	1.113	1.008	3.595	0.218	1.061	106.31	3.606
5O8O5	A	136	6.932	1.387	9.642	−2.055	−0.426	1.089	0.723	3.562	0.219	1.062	87.18	3.299
5O9O5	Iso	136	12.647	1.113	3.887	−1.245	−0.641	1.119	1.477	4.212	0.192	1.046	131.05	6.157
5O9O5	N	116	8.864	1.204	5.196	−1.475	−0.568	1.121	1.251	3.736	0.211	1.057	110.40	4.265
5O10O5	Iso	156	8.684	1.213	5.340	−1.498	−0.561	1.121	1.229	3.715	0.212	1.057	120.32	4.175
5O10O5	N	140	7.472	1.301	7.158	−1.760	−0.492	1.111	0.985	3.589	0.218	1.061	101.54	3.569
5O11O5	Iso	129	9.431	1.182	4.833	−1.415	−0.585	1.121	1.309	3.804	0.208	1.055	117.68	4.549
5O12O5	Iso	141	8.086	1.248	5.984	−1.596	−0.533	1.118	1.136	3.648	0.215	1.059	110.43	3.876
6O5O6	Iso	140	8.699	1.212	5.327	−1.496	−0.562	1.121	1.231	3.717	0.212	1.057	115.95	4.183
6O5O6	A	130	7.352	1.316	7.514	−1.806	−0.481	1.109	0.943	3.580	0.218	1.061	96.86	3.509
6O6O6	Iso	185	8.339	1.231	5.674	−1.550	−0.546	1.120	1.180	3.676	0.214	1.058	125.08	4.003
6O6O6	A	165	7.654	1.283	6.719	−1.701	−0.506	1.114	1.039	3.605	0.217	1.060	110.87	3.661
6O6O6	G	130	7.352	1.316	7.514	−1.806	−0.481	1.109	0.943	3.580	0.218	1.061	96.86	3.509
6O12O6	Iso	137.2	6.978	1.376	9.295	−2.017	−0.434	1.093	0.756	3.562	0.219	1.062	89.03	3.322
6O12O6	N	130	6.858	1.406	10.339	−2.128	−0.412	1.082	0.659	3.564	0.219	1.061	82.96	3.262
7O4O7	Iso	214	6.875	1.401	10.164	−2.110	−0.415	1.084	0.675	3.563	0.219	1.061	101.12	3.271
7O4O7	N	163	7.665	1.282	6.696	−1.698	−0.507	1.114	1.042	3.606	0.217	1.060	110.54	3.666
7O5O7	Iso	147	7.060	1.360	8.765	−1.958	−0.447	1.098	0.808	3.564	0.219	1.061	93.80	3.363
7O5O7	N	92	8.147	1.243	5.902	−1.584	−0.537	1.119	1.147	3.655	0.215	1.059	97.96	3.907
7O6O7	Iso	188.9	6.843	1.410	10.506	−2.146	−0.408	1.080	0.645	3.565	0.219	1.061	94.32	3.255
7O6O7	N	182	6.753	1.442	11.830	−2.274	−0.384	1.066	0.535	3.575	0.219	1.061	87.46	3.210
7O6O7	A	176	6.659	1.500	14.898	−2.536	−0.340	1.033	0.317	3.608	0.217	1.060	76.42	3.163
7O12O7	Iso	137.9	6.975	1.377	9.310	−2.019	−0.434	1.093	0.754	3.562	0.219	1.062	89.11	3.321
7O12O7	N	131	6.856	1.407	10.366	−2.131	−0.411	1.082	0.657	3.564	0.219	1.061	83.06	3.261
8O12O8	Iso	135.4	6.983	1.375	9.254	−2.013	−0.435	1.093	0.760	3.562	0.219	1.062	88.83	3.325
8O12O8	N	128	6.863	1.404	10.284	−2.123	−0.413	1.083	0.664	3.564	0.219	1.061	82.77	3.265
10O4O10	Iso	210.8	6.882	1.399	10.094	−2.103	−0.417	1.085	0.681	3.563	0.219	1.062	100.80	3.274
10O4O10	N	162.3	7.669	1.281	6.687	−1.696	−0.507	1.114	1.043	3.606	0.217	1.060	110.43	3.668
10O10O10	Iso	148.1	7.431	1.306	7.272	−1.775	−0.488	1.110	0.972	3.586	0.218	1.061	102.77	3.549
10O10O10N	N	140.2	7.084	1.356	8.631	−1.942	−0.450	1.099	0.822	3.565	0.219	1.061	92.97	3.376
10O12O10	Iso	137	7.819	1.268	6.398	−1.656	−0.518	1.116	1.080	3.621	0.216	1.060	106.13	3.743
10O12O10N	N	131	7.347	1.316	7.529	−1.808	−0.480	1.108	0.942	3.579	0.218	1.061	97.01	3.507

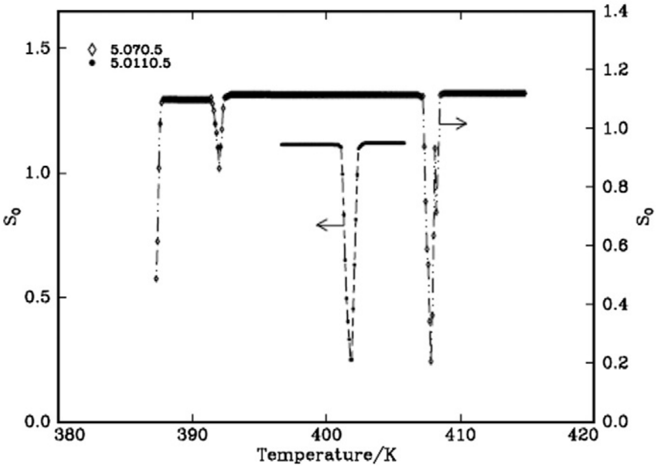


Fig. 1. Variation of Sharma parameter (S_0) with temperature in 5.070.5 and 5.0110.5 compounds.

where

$$Y = \left(36\pi N {V_0}^2\right)^{1/3}. \tag{17b}$$

The molar volume at 0 K (V_0) can be obtained by also as

$$V_0 = \frac{V}{V^{\sim}}. \tag{18}$$

N is the Avogadro number and $V^{\sim}$ is taken from Eq. (2).

Further, V_0 can be obtained directly from molar volume data by extrapolating isotropic data to 0 K.

3.2. Molecular radius (M_r)

M_r for the LC molecule can be obtained from density and refractive index results and the relevant expressions are given below [25]

(i). From density, ρ

$$M_r = \frac{1}{2}3\sqrt{\frac{M\sqrt{2}}{\rho N}} \tag{19}$$

where M is the molecular weight.

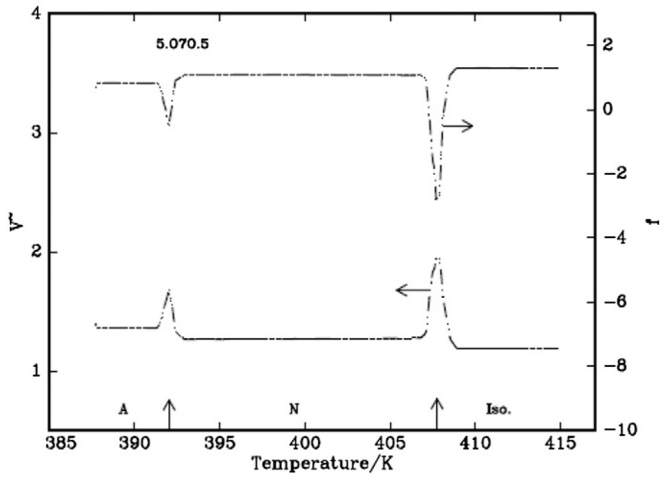


Fig. 2. Variation of reduced volume ($V^{\sim}$) with temperature in 5.070.5 compound.

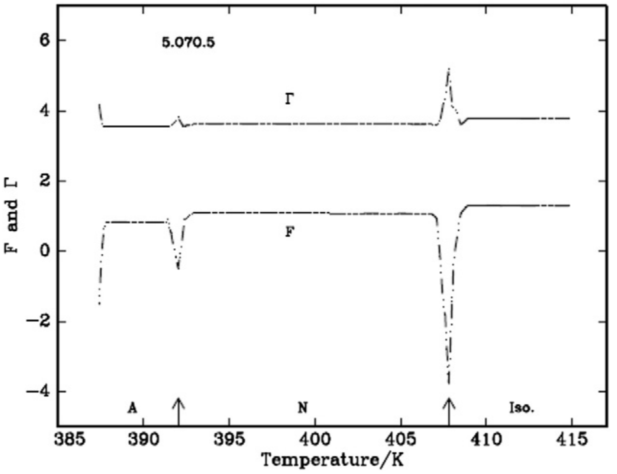


Fig. 3. Variation of Huggins parameter (F) and isothermal microscopic Gruneisen parameter (Γ) with temperature in 5.070.5 compound.

(ii). The refractive index data can be utilized in conjunction with molar volume to compute the molecular radius (M_r) using the following relation [25,26]

$$M_r = \left[\left(\frac{3}{4\pi N}\right)\frac{(n^2-1)}{(n^2+2)}V_m\right]^{1/3} \tag{20}$$

3.3. Acoustic nonlinearity parameter, B/A

There are a number of reports in literature describing in detail the theoretical and empirical approach for the estimation of B/A from α and u, sound velocity respectively, the relevant expressions of the non-linearity parameter, B/A is given as [26,27]

$$B/A = 2u\rho[du/dp]_T. \tag{21}$$

General formalism for B/A in terms of the acoustical parameters for liquids and polymers has been made using Moelwyns–Hughes parameter (C1), isobaric acoustic parameter (K) and the isothermal acoustic parameter (K″) (the detailed method of calculation of K and K″ from

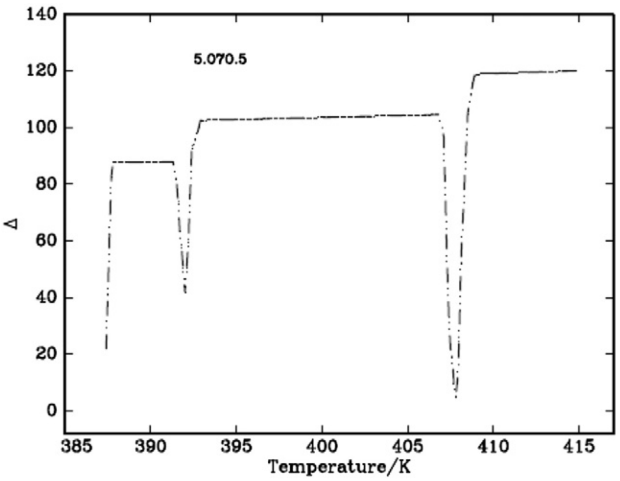


Fig. 4. Variation of isochoric acoustical parameter (Δ) with temperature in 5.070.5 compound.

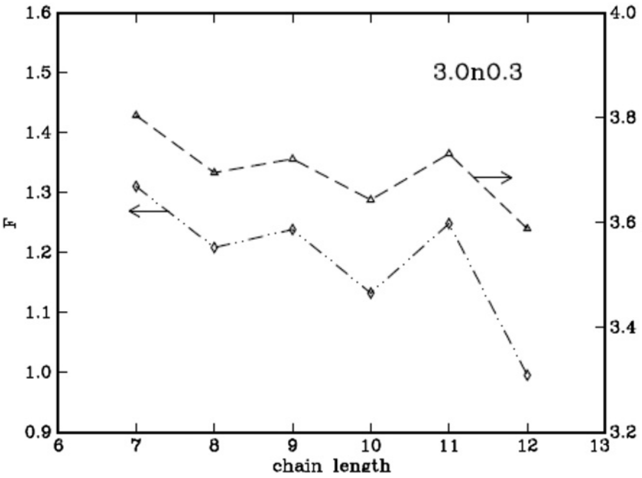


Fig. 5. Variation of Huggins parameter (*F*) with chain number in 3.OnO.3 compounds.

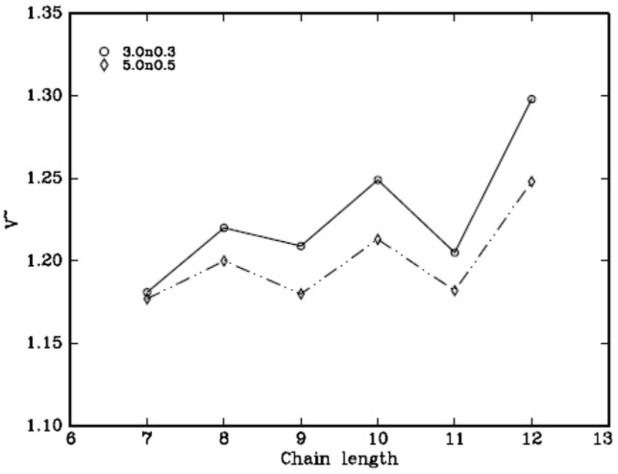


Fig. 7. Variation of reduced volume ($\tilde{V}$) with chain number in 3.OnO.3 and 5.OnO.5 compounds.

α is given elsewhere [27] obtained from the thermal expansion coefficient, α, and from the sound velocity, u respectively. The expressions for B/A from density are given as [25,26].

$$B/A = C_1 - 1 \tag{22a}$$

$$B/A = 2K + 2\gamma K'' \tag{22b}$$

4. Results and discussion

The symmetric dimeric liquid crystal compounds α,ω–bis-(4-n-alkylaniline benzylidene – 4' –oxy) alkanes, referred to as m.OnO.m with m = 3, 4, 5, 6, 7, 8 and 10 and n = 4, 5, 6, 7, 8, 9, 10, 11 and 12 are considered in the present study.

The relevant data of the thermal expansion coefficient (α) which is obtained from density results is taken from the literature [27,28].

The variation of the thermodynamic parameters such as Moelwyn-Hughes (C_1), reduced volume($\tilde{V}$), reduced compressibility($\tilde{V}^{C1}$), isochoric temperature coefficient of internal pressure (X), Sharma Parameter (S_0), Isothermal microscopic Gruneisen parameter (Γ), Gruneisen parameter (Γ_p), isothermal (Γ_{ith}), isobaric (Γ_{iba}) and isochoric (Γ_{ich}) Gruneisen parameters, available volume (V_a), intermolecular freelength (L_f), molecular radius (M_r) and nonlinearity parameter (B/A) etc. with temperature, phase variants, spacer length and terminal groups.

The dimensionless thermodynamic parameter C_1, defined as the pressure coefficient of bulk modulus as introduced by Moelwyn-Hughes [10], serves as severe test for the equation of state for liquids and solids and liquid crystals [29–31]. The calculated values of the Moelwyn–Hughes parameter C_1 for the materials are presented in Table 1 in both isotropic and LC phases. It is already known that C_1 offers the simplest scale for the determination of molecular ordering, structure, interactions and anharmonicity in some materials [32]. Further, C_1 signifies the nonlinear variation with temperature. It is quite interesting to note that $(B/A) + 1 = C_1$. The ratio of $C_1/(B/A)$ is approximately equal to unity which is true in our case as well as in other LC materials also [33–35].

The isobaric Gruneisen parameter Γ_{iba} is found to be less than the isothermal Gruneisen parameter Γ_{ith}. This trend is similar in the case of these materials except in the vicinity of phase transition. The fractional free volume (Va/V) determines the disorder, which is due to increased mobility of the molecules in a system. It is found that the fractional free volume behaves like that of the thermal expansion coefficient. For most of the materials under present investigation, the fractional free volume V_a/V_0 values are around 0.23, which are of the same order as observed for saturated hydrocarbons and other liquids and liquid crystals [36].

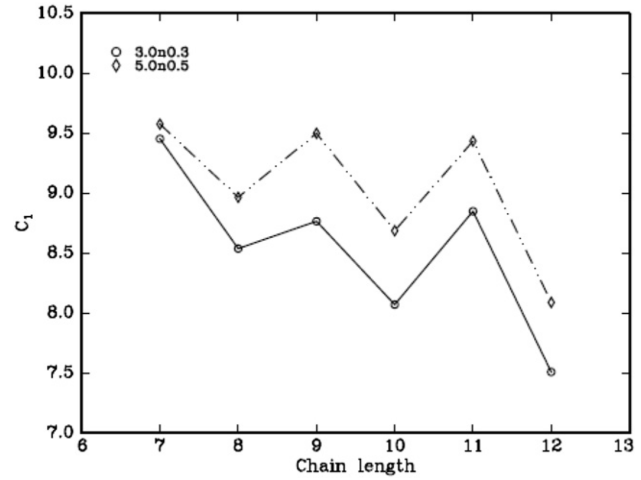


Fig. 6. Variation of Moelwyn–Hughes (C_1) with chain number in 3.OnO.3 and 5.OnO.5 compounds.

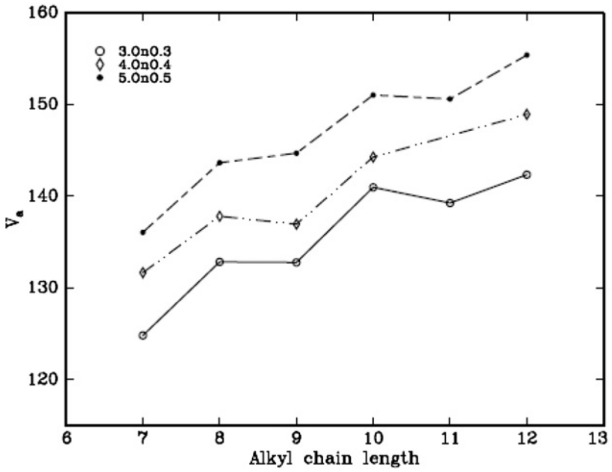


Fig. 8. Variation of available volume (V_a) with chain number in 3.OnO.3, 4.OnO.4 and 5.OnO.5 compounds.

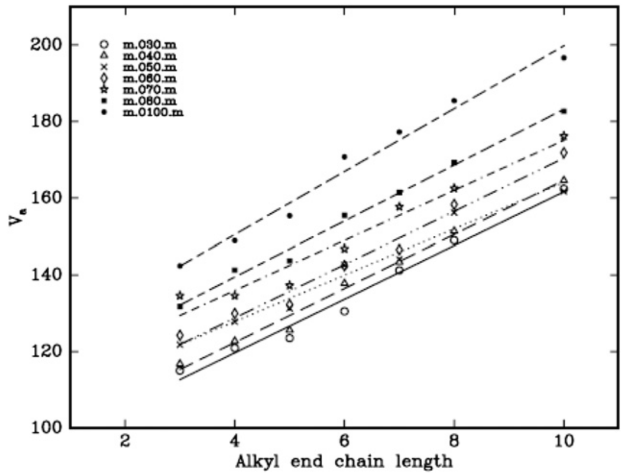


Fig. 9. Variation of available volume (V_a) with chain number in m.O3O.m, m.O4O.m, m.O5O.m, m.O6O.m, m.O7O.m, m.O8O.m and m.O10O.m compounds.

The variation of all the thermodynamic parameters in different mesomorphic phases including isotropic phase for all the compounds (whose density data is available) is depicted in Table 1. It is observed that all the parameters exhibit an odd even or even odd effect either with n or m. Further, all the parameters show slight variation in their magnitude in different phases at either higher or lower values depending upon whether a particular parameter is directly or indirectly proportional to α as in the case of monomers [1]. The parameters C_1, X', F, Γ, Δ, Γ_p and their variation with temperature show decrease with the decrease of temperature i.e., exhibiting low values in liquid crystalline phases compared to the isotropic phase which shows that the molecular ordering increases as the temperature decreases in liquid crystal phases which is same trend as in the case of monomers [17]. Fig. 1 depicts the variation of Sharma parameter, S_0 with temperature in 5.O7O.5 and 5.O11O.5 compounds. It is observed from the Fig. 1 that S_0 exhibits variation within the vicinity of phase transition and remains its magnitude constant throughout the temperature range irrespective of the variation of terminal chain or spacer length suggesting its independency with the nature of the material which is in agreement with the earlier reports [18]. The temperature variation of the parameters Δ, F, $\tilde{V}$, f and Γ in 5.O7O.5 are shown in Figs. 2 to 4. All the parameters exhibit either dip or elevation at the phase transformation. However, the values of these parameters remain constant in any particular phase.

Fig. 5 shows the variation of Huggins parameter (F) and isothermal microscopic Gruneisan parameter (Γ) with chain number in the case of 3.OnO.3 compounds in the isotropic phase. It is observed that the variation is found to exhibit odd–even effect which is in contrary to that found in 5O.m [18] compounds where even–odd effect predominates.

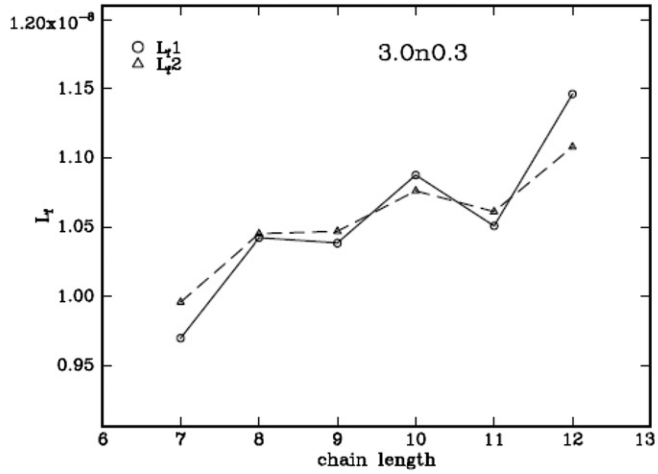


Fig. 10. Variation of molecular free length (L_f) estimated in two different ways with chain length in 3.OnO.3 compounds.

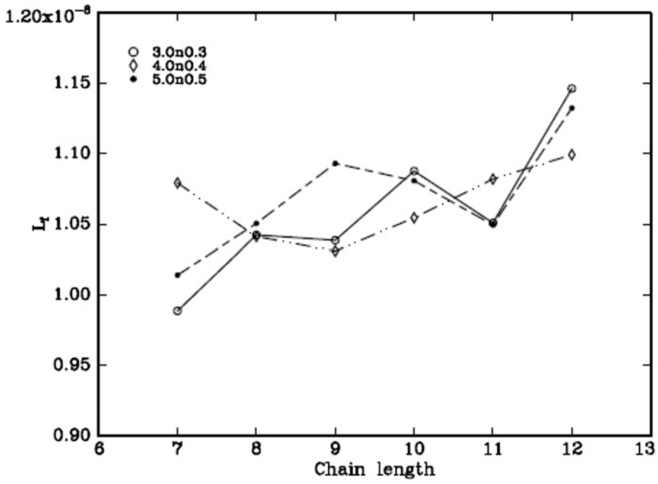


Fig. 11. Variation of molecular free length (L_f) with chain length in 3.OnO.3, 4.OnO.4 and 5.OnO.5 compounds.

The Fig. 6 shows the odd-even variation of Moelwyn–Hughes parameter, C_1 with the spacer chain number in 3.OnO.3 and 5.OnO.5. The Fig. 7 exhibits an opposite even –odd effect in the case of above two compounds for the parameter $\tilde{V}$, the reduced volume. As already stated the odd–even or even–odd effect with the chain numbers depends whether the parameter is directly or indirectly proportional to the volume expansion, α.

4.1. Available volume and Intermolecular free length

The variation of available volume V_a which is estimated is found to show an even odd trend when the central spacer length which is shown in Fig. 8. When the terminal alkyl chains varied it showed a linear variation which is depicted in Fig. 9. The increment per methylene unit is found to be around 3 units with spacer length whereas it is double with the terminal alkyl chains.

The intermolecular free length (L_f) obtained from both the methods are found to be in agreement with each other and is evident from Fig. 10 which represents the variation of intermolecular freelength (L_f) with chain number in isotropic phase obtained from two methods in 3.OnO.3 compounds. Further, the variation of L_f in isotropic phase is shown in Fig. 11 for 3.OnO3, 4.OnO.4 and 5.OnO.5 compounds. It is found from the Figure that L_f exhibiting an odd even effect with variation of central spacer length.

5. Molecular radius (M_r)

The molecular radius M_r is estimated for all the compounds from the density data and refractive index data. The core radius and the increment per methylene unit in all the compounds of different homologous

Table 2
The core radius (Å) and increment with CH_2 unit in various compounds of symmetric DLC with the variation of spacer length.

Compound	M_r (Å) increment per CH_2	Core M_r (Å)
3.OnO.3	0.0494	5.276
4.OnO.4	0.0494	5.368
5.OnO.5	0.0468	5.469
6.OnO.6	0.0437	5.596
7.OnO.7	0.0440	5.670
8.OnO.8	0.0429	5.773
10.OnO.10	0.0412	5.946

Table 3
The core radius (Å) and increment with CH_2 unit in various compounds of symmetric DLC with the variation of terminal alkylchain length.

Compound	M_r (Å) increment per CH_2	Core M_r (Å)
m.O2O.m	0.0950	5.085
m.O3O.m	0.0930	5.146
m.O4O.m	0.0918	5.202
m.O5O.m	0.0903	5.259
m.O6O.m	0.0895	5.313
m.O7O.m	0.0859	5.383
m.O8O.m	0.0863	5.422
m.O9O.m	0.0855	5.471
m.O10O.m	0.0844	5.518
m.O11O.m	0.0828	5.574
m.O12O.m	0.0821	5.620

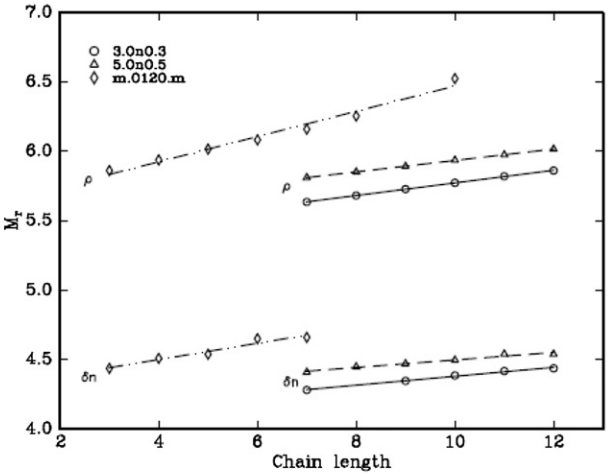


Fig. 13. Variation of molecular radius (M_r) with chain length estimated from density and refractive index data in 3.OnO.3, 5.OnO.5 and m.O12O.m compounds.

series with spacer length and terminal alkyl chain length are given in Tables 2 and 3 respectively. The percentage of errors between the M_r calculated from density and refractive index is roughly the same in dimers and the corresponding errors in monomers it is around 22 to 24%. The variation of M_r obtained from density and refractive index is depicted in Fig. 12 for the case of 3.OnO.3, 5.OnO.5 and m.O12O.m. Fig. 13 represents the variation of refractive index with chain number in isotropic phase for all the series of compounds. The molecular radius estimated using α is about √2 times that is obtained from δn which is the same cases as that in the case of corresponding monomers also [18].

6. Nonlinearity parameter (*B/A*)

The nonlinearity parameter is obtained from Eq. (2) in two different ways. The variation of with the chain length is depicted in Fig. 14. The *B/A* value decreases with increase in molecular weight with an even–odd fashion, but the magnitude of variation is from 5.5 to 9. Generally this parameter lies in the range 5–12, with extreme variations of 2 and 13. These extreme values are reported in some cases [29].

The salient features from the study are (figures and tables)

1. The variation of all the parameters in a particular phase and also through the total DLC molecule is showing the same trend as in the case of monomers.
2. The Huggins, F is found to exhibit (with the chin number) odd–even effect which is in contrary to that found in 5O.m compounds where even-odd effect predominates,
3. the parameters C_1, X', F, Γ, Δ, Γ_p and their variation with temperature show decrease with the decrease of temperature i.e., exhibiting low values in liquid crystalline phases compared to the isotropic phase which shows the molecular ordering increases as the temperature decreases in liquid crystal phases which is same trend as in the case of monomers, the parameters Δ, F, $\tilde{V}$, f and Γ_{i} exhibit either dip or elevation at the phase transformation. However, the values of these parameters remain constant in any particular LC phase,
4. the available volume V_a is found to show an even odd trend when the central spacer length which is shown in Fig. 8. When the terminal alkyl chains varied it showed a linear variation which is depicted in Fig. 9. The increment per methylene unit is found to be around 3 units with spacer length whereas it is double with the terminal alkyl chains,
5. S_0 exhibits variation within the vicinity of phase transition and remains its magnitude constant throughout the temperature range irrespective of the variation of terminal chain or spacer length suggesting its independency with the nature of the material which is in agreement with the earlier reports,
6. the molecular free length, L_f exhibits an odd even effect with variation of central spacer length,
7. the percentage of errors between the M_r calculated from density and refractive index is roughly same in dimers and the corresponding monomers and is around 22 to 24%.
8. From Fig. 14. The *B/A* value decreases with increase in molecular weight with an even–odd fashion, but the magnitude of variation is from 5.5 to 9. Generally this parameter lies in the range 5–12, with

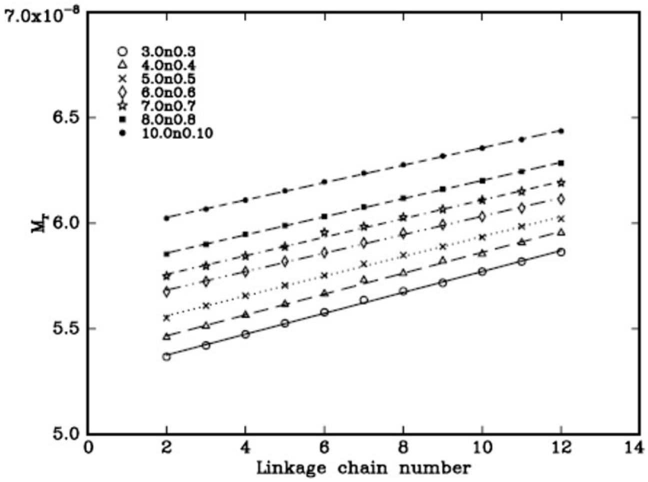


Fig. 12. Variation of molecular radius (M_r) with chain length in m.OnO.m where m = 3,4,5,6,7,8 and 10 and n = 2 to 12.

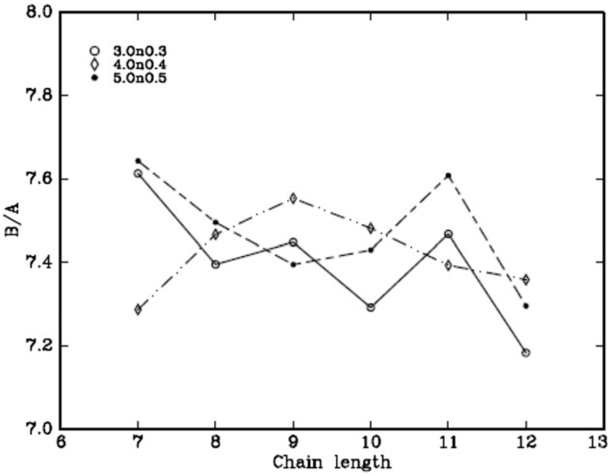


Fig. 14. Variation of nonlinearity parameter (*B/A*) with chain length in 3.OnO.3, 4.OnO.4 and 5.OnO.5 compounds.

extreme variations of 2 and 13. These extreme values are reported in some cases.

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